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(54) Title: PHOSPHORUS COMPOUNDS AS CORROSION INHIBITORS FOR PERFLUOROPOLYETHERS (57) Abstract Novel phosphorus compounds are effective corrosion inhibitors for perfluoropolyether lubricating oils and greases, and hydraulic fluids.		

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TITLE

PHOSPHORUS COMPOUNDS AS CORROSION INHIBITORS FOR PERFLUOROPOLYETHERS

BACKGROUND OF THE INVENTION**5 FIELD OF INVENTION**

This invention relates to novel organic phosphorus compounds. The compounds have general utility as surfactants and particular utility as an additive to perfluoropolyether compositions, including oil and grease lubricants, to inhibit corrosion and rust of metals in contact with the compositions.

10 DESCRIPTION OF RELATED ART

Perfluoropolyethers have excellent thermal and oxidative stability and are used as greases, hydraulic fluids, and oils for service under extreme or demanding conditions wherein more conventional oils and greases are not adequate, for instance at temperatures above 260°C and up to 370°C to 425°C, depending on the particular oil or grease. These oils and greases are available from a number of commercial sources, including E. I. du Pont de Nemours that markets them under the Krytox® trademark.

While the perfluoropolyethers *per se* are highly stable, they are highly permeable to oxygen and moisture. Thus, the oil and grease do not form an effective barrier against rust and corrosion of metallic parts they contact. As used herein, the term "corrosion" refers to the oxidation of metal in contact with oxygen, and the term "rust" refers to the oxidation of metal in contact with water.

Sodium nitrite conventionally has been added as a corrosion inhibitor to some perfluoropolyether greases. Sodium nitrite is not soluble in perfluoropolyether oils. In the greases, it is present as a particulate dispersion. Ideally, a rust and corrosion inhibitor would be present in solution to provide better protection and to eliminate the potential problem of separation from the oil or grease.

Many organic phosphorus compounds have been suggested in the patent literature as rust and/or corrosion inhibitors for perfluoropolyether oils and greases. For example, U.S. Patent 3,306,855 to Borecki proposes a perfluoroalkyl ether phosphate containing at least one acidic hydrogen, and U.S.

- 5 Patent 5,550,277 to Paciorek et al., proposes a variety of fully and partially esterified phosphates and phosphates, some of which are acidic.

Other candidate rust and corrosion inhibitors proposed in the art are very difficult or expensive to synthesize. For example, some of the proposed additives contain large quantities of costly perfluoroalkyl substituents. Others, such as some
10 of the partially esterified phosphates proposed by U.S. Patent 5,550,277, require formation of an intermediate fluoroether-substituted phenol that is very difficult to synthesize in a commercial manufacturing process.

The use of acidic rust and corrosion inhibitors is contraindicated in admixture with perfluoropolyether greases containing the common sodium nitrite
15 inhibitor, since the acidic group may react with the sodium nitrite to generate noxious nitrogen oxides. Since the presence of greases containing sodium nitrite inhibitors has been pervasive, and they are expensive to replace, there is a high probability that new greases and oils will be placed in existing equipment lubrication reservoirs containing sodium nitrite.

20 Thus, there is an ongoing need for new corrosion and rust inhibitor additives for perfluoropolyether compositions, including oils and greases.

SUMMARY OF THE INVENTION

This invention provides novel partially and fully esterified aryl phosphorus compounds that are (i) soluble or form stable dispersions in perfluoropolyethers, or
25 (ii) compatible with sodium nitrite present in many commercial perfluoropolyether greases. The novel compounds provide excellent rust and corrosion resistance to metals that contact the perfluoropolyether. The compounds are readily synthesized and relatively inexpensive in that some of the perfluoroalkyl substitution in prior art compounds is replaced with aryl and aryloxy substituents, providing the desired

functionality of prior additives with less expensive substituents. More particularly the invention provides:

5 **Class A:** Partially esterified aryl phosphates and phosphonates, and salts thereof, containing either (i) a mono- or poly-alkylene oxide linking group between the phosphorus and a fluorocarbon group, or (ii) no linking group between the phosphorus and fluorocarbon group;

10 **Class B:** Asymmetrical fully substituted compounds being either (i) aryl phosphites or phosphates containing a mono or poly alkylene oxide linking group between the phosphorus and a perfluoroether group, or (ii) aryl phosphines; phosphinites, phosphonites, phosphine oxides, phosphinates or phosphonates with no linking group between the phosphorus and a fluorocarbon group; and

15 **Class C:** Salts of partially esterified aryl phosphates having an aryl group between the phosphorus and a fluorocarbon.

These novel compounds have general utility as surfactants, and particular utility as corrosion and rust inhibitors in perfluoropolyether compositions such as oils and greases.

20

DETAILED DESCRIPTION OF THE INVENTION

The novel phosphorus compounds of the invention are represented by the following definitions:

25 **Class A:** Partially esterified aryl phosphates and phosphonates, and salts thereof, containing either (i) a mono- or poly-alkylene oxide linking group between the phosphorus and a fluorocarbon group, or (ii) no linking group between the phosphorus and fluorocarbon group;

Class B: Asymmetrical fully substituted compounds being either (i) aryl phosphites or phosphates containing a mono or poly alkylene oxide linking group between the phosphorus and a perfluoroether group, or (ii) aryl phosphines, phosphinites, phosphonites, phosphine oxides, phosphinates or phosphonates with no linking group between the phosphorus and a fluorocarbon group; and

Class C: Salts of partially esterified aryl phosphates having an aryl group between the phosphorus and a fluorocarbon.

Specific compounds within the three classes will be described first. Then, convenient synthesis techniques will be described.

CLASS A:

Representative compounds within Class A have the following formulae:

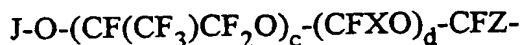
Class A(i) compounds having a mono or poly alkylene oxide linking group:

- (Formula I) $[Rf-Y]_{(2-x)}-P(E)-[O_bC_6R_5][OM]_x$
 (Formula II) $[Rf'-Y]_{(2-x)}-P(E)-[O_bC_6R_5][OM]_x$
 (Formula III) $[MO]_x[C_6R_5O_b]-P(E)-Y-Rf''-Y-P(E)-[O_bC_6R_5]_{(2-x)}[OM]_x$

where:

- Y is $(CH_2)_zO(CH_2CH_2O)_{z'}$, wherein z is 1 to 4 and z' is 0, 1 or 2,
 x is 0.05 to 1,
 E is oxygen or sulfur,
 b is 0 or 1,
 R is the same or different substituent chosen from hydrogen, halogen, alkyl, aryl, nitro, cyano, alkoxy, primary and secondary amino, sulfonyl, carboxyl, or phenoxy, and
 M is hydrogen, alkali metal, alkaline earth metal, or ammonium.

Rf is a polyether chain having a molecular weight ranging from 400 to 15,000 and composed of repeating units selected from the group consisting of:



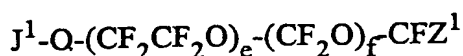
where:

J is a fluoroalkyl group selected from the group consisting of -CF₃, -C₂F₅, -C₃F₇, -CF₂Cl, -C₂F₄Cl, and -C₃F₆Cl,

5 X is -F or -CF₃,

Z is -F, -Cl or -CF₃, and

c and d are numbers such that the c/d ratio ranges from 0.01 to 0.5, and the molecular weight ranges from 400 to 15,000;



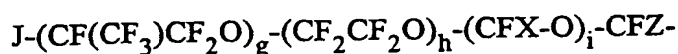
10 where:

J¹ is a fluoroalkyl group selected from the group consisting of -CF₃, -C₂F₅, -CF₂Cl, and -C₂F₄Cl,

Z¹ is -F or -Cl, and

e and f are numbers such that the e/f ratio ranges from 0.5 to 2 and, the molecular weight ranges from 400 to 15,000;

15



where:

J and X are as defined above,

Z is -F, -Cl, or -CF₃, and

20

g, h and i are numbers such that (g+h) ranges from 1 to 50, the i/(g+h) ratio ranges from 0.1 to 0.05, and the molecular weight is from 400 to 15,000;

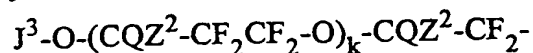


where:

J² is -C₂F₅ or -C₃F₇, and

25

j is a number such that the molecular weight ranges from 400 to 15,000;



where:

J^3 is selected from the group consisting of $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, and $-\text{C}_3\text{F}_7$,

Q and Z^2 , equal or different, are F, Cl or H, and

k is a number such that the molecular weight ranges from 400 to 15,000;

5 and J^4 -O-($\text{CF}_2\text{CF}_2\text{O}$)_l- CF_2 -

where:

J^4 is $-\text{CF}_3$, or $-\text{C}_2\text{F}_5$ and

l is a number such that the molecular weight ranges from 400 to 15,000; or

Rf' is Z^2 -(CF_2)_m-

10 where:

Z^2 is H, F, or Cl and

m has a value from 2 to 20; or

Rf" is a perfluoropolyether chain having a number average molecular weight of 500 to 15,000, selected from the group consisting of:

15 (i) $(\text{CF}_2\text{CF}_2\text{O})_n$ -(CF_2O)_o- CF_2 -

wherein the units with formulae $\text{C}_2\text{F}_4\text{O}$ and CF_2O are randomly distributed along the chain, and n and o are integers, whose ratio, n/o, is in the range of from 0.3 to 5;

(ii) $-(\text{C}_3\text{F}_6\text{O})_p$ -($\text{CF}_2\text{CF}_2\text{O}$)_q-(CFXO)_r- CF_2 -

20 wherein

X is F or CF_3 and

p, q and r are numbers such that (p+q) ranges from 1 to 50, and the r/(p+q) ratio ranges from 0.1 to 0.05, and the molecular weight is from 400 to 15,000; and

25 (iii) $-((\text{CQZ}^2)\text{CF}_2\text{CF}_2\text{O})_s$ - CF_2 - CF_2 -

where

Q and Z^2 , equal or different, are F, Cl or H, and

s is a number such that the molecular weight ranges from 400 to 15,000.

Representative compounds within Class A(i) include:

For Formula I; $F(CF(CF_3)CF_2O)_n CF(CF_3)CH_2OP(O)[OH]C_6H_5$

and

5 $F(CF(CF_3)CF_2O)_n CF(CF_3)CH_2OP(O)[OH]OC_6H_5$

where n is 4 to 10.

For Formula II; $F(CF_2)_m CH_2CH_2OP(O)[OH]C_6H_5$

and

$F(CF_2)_m CH_2CH_2OP(O)[OH]OC_6H_5$

10 where m is 4, 6 or 8.

For Formula III; $[HO](C_6H_5)P(O)OCH_2-(CF_2CF_2O)_n-(CF_2O)_o-CF_2-CH_2OP(O)(C_6H_5)[OH]$

and

$[HO](H_5C_6O)P(O)OCH_2-(CF_2CF_2O)_n-(CF_2O)_o-CF_2-CH_2OP(O)(OC_6H_5)[OH]$

where $(n+o) = 8$ and $n/o = 1$.

15 **Class A(ii)** compounds having a mono or poly alkylene oxide linking group:

(Formula IV) $[Rf-]_{(2-x)}-P(E)-[O_b-C_6R_5] [OM]_x$

(Formula V) $[Rf'-]_{(2-x)}-P(E)-[O_bC_6R_5] [OM]_x$

(Formula VI) $[MO]_x[C_6R_5O_b]_{(2-x)}-P(E)-Rf''-P(E)-[O_bC_6R_5]_{(2-x)} [OM]_x$

20 wherein Rf, Rf', Rf'', x, E, b, R, and M are as previously defined for Formulae I to III.

Representative compounds within Class A(ii) include:

For Formula IV; $F(CF(CF_3)CF_2O)_nCF(CF_3)P(O)[OH]C_6H_5$

and

$F(CF(CF_3)CF_2O)_nCF(CF_3)P(O)[OH]OC_6H_5$

5 where n is 4 to 10.

For Formula V; $F(CF_2)_mP(O)[OH]C_6H_5$

and

$F(CF_2)_mP(O)[OH]OC_6H_5$

where m is 4, 6 or 8.

10 For Formula VI; $[HO](C_6H_5)P(O)-(CF_2CF_2O)_n-(CF_2O)_o-CF_2-P(O)(C_6H_5)[OH]$

and

$[HO](H_5C_6O)P(O)-(CF_2CF_2O)_n-(CF_2O)_o-CF_2-P(O)(OC_6H_5)[OH]$

where (n+o) is 8, and n/o is 1

CLASS B:

15 Representative compounds within Class B have the following formulae:

Class B(i) compounds having a mono or poly alkylene oxide linking group:

(Formula VII) $[Rf-Y-]_{(3-y)}-P(E)_a-[O-C_6R_5]_y$

(Formula VIII) $(C_6R_5O)_2-P(E)_a-Y-Rf"-Y-P(E)_a-(OC_6R_5)_2$

wherein R, Rf, Y, and E are as previously defined and y is 0.05 to 2,

20 and a is 0 or 1.

Representative compounds within Class B(i) include:

For Formula VII; $[F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2O]P(OC_6H_5)_2$

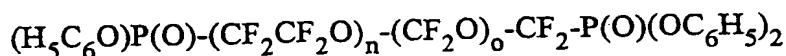
and

$[F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2O]_2P(O)(OC_6H_5)$

25 where n is 4 to 10.

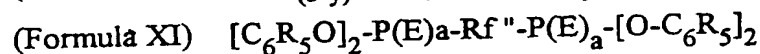
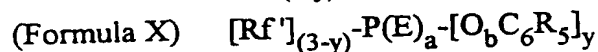
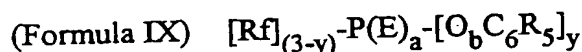
For Formula VIII; $(\text{H}_5\text{C}_6\text{O})_2\text{P}-(\text{CF}_2\text{CF}_2\text{O})_n-(\text{CF}_2\text{O})_o-\text{CF}_2-\text{P}(\text{OC}_6\text{H}_5)_2$

and



where n is (n+o) is 8, and n/o is 1.

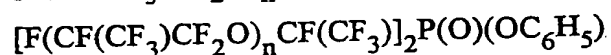
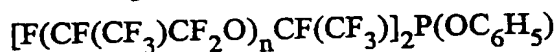
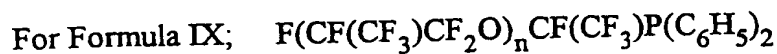
5 **Class B(ii)** compounds not having a polyalkylene oxide linking group:



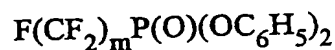
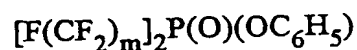
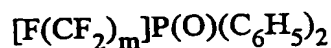
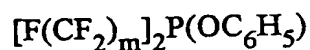
wherein

10 Rf , Rf' , Rf'' , a, b, E, R, y, and n are as previously defined for Formulae I to VIII.

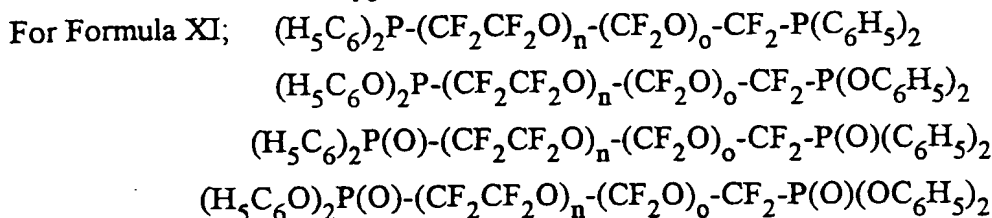
Representative compounds within Class B(ii) include:



where n is 4 to 10.



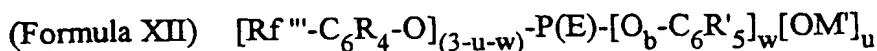
where m is 4, 6 or 8.



5 where (n+o) is 8; and n/o is 1.

CLASS C:

Representative compounds within Class C have the following formulae:



wherein

10 Rf''' is Rf' or Rf'' , and Rf' , Rf'' , E, b, and R are as previously defined for Formulae I to III.

M' is an alkali metal, alkaline earth metal, or ammonium, and

u and w are the same or different between 0 and 1, and

R' is an aryl group.

15 Examples of R groups include phenyl and substituted phenyl, $\text{C}_6\text{H}_4-\text{R}''$, in which R'' is an aromatic, alkyl, or thioaryl (SC_6H_5).

SYNTHESIS

Compounds of Class A(i) and B(i)

Syntheses of the additives of the invention are accomplished by the method
 20 described by Moreton in U.S. 2,694,083 by reaction of either (a) aryloxy substituted or aryl substituted phosphorus oxychlorides at elevated temperatures with a fluoroalcohol of the formula $\text{Rf}-\text{OH}$, or (b) with the corresponding fluoroalkyl phosphorus dichloride and a substituted phenol. Alternately, the products are prepared by mixing said reactants in the presence of a dry aprotic
 25 organic base such as triethylamine or pyridine, and allowing the reaction to proceed at room temperature until complete either with or without solvent as described by Paciorek in U.S. 5,550,277. Control over the specific reaction

products is by stoichiometry. This reaction is followed by hydrolysis to form the corresponding acid ester. Additionally, the products are neutralized with a solution or suspension of the hydroxide or carbonate of the alkali metal or alkaline earth metal, or ammonium hydroxide solution, prior to isolation to provide the
5 corresponding salt, producing a rust and corrosion prevention additive compatible with perfluoropolyether oils and greases containing sodium nitrite. The solution is washed with water to remove excess acid and salts or base and salts, then vacuum stripped to remove solvents and volatiles.

Compounds of Class A(ii) and B(ii)

10 Those compounds are prepared by reacting a perfluoro alkyl or perfluoroether iodide with elemental phosphorus at elevated temperatures. The isolated diiodo phosphine can either be reacted with a metalated aryl or aryloxy compound preparing the corresponding phosphorus(III) compounds. Oxidation with chlorine/water or hydrogen peroxide gives the phosphorus(V) oxide.
15 Oxidation of the phosphorus(III) with chlorine followed by treatment with H₂S or Na₂S gives the thiophosphorus(V) materials.

Compounds of Class C

Syntheses of the perfluoropolyether additives of Formula XI and XII are accomplished as described by Paciorek et al. in US 5,550,277 cited above, except
20 that the final products of Paciorek et al. are neutralized with a solution of suspension of the hydroxide or carbonate of the alkali metal or alkaline earth metal, or ammonium hydroxide solutions prior to isolation to provide the corresponding salt, producing a rust and corrosion prevention additive compatible with perfluoropolyether oils and greases containing sodium nitrite.

25

USE OF THE PHOSPHORUS COMPOUNDS AS RUST AND CORROSION INHIBITORS

The phosphorus compounds of the present invention constitute new anticorrosion and antirust additives effective in all perfluoropolyether lubricants. These new additives are variously soluble or dispersible in the perfluoropolyether

oil and provide antirust and anticorrosion protection to the oil thereby improving wear of parts lubricated or in contact with the oil. The alkali metal, alkaline earth metal, or ammonium salts of the partially esterified phosphorus compound additives either allow sodium nitrite to be replaced or, since they are compatible with the sodium nitrite, provide the option to retain sodium nitrite in the formulation. The present invention further provides perfluoropolyether oils, greases, and fluids containing an effective amount of the inhibitor.

By the term "effective amount" is meant the amount required to produce a useful level of inhibition for the required service life of the device containing the oil or grease at the operating temperature. Various metals differ considerably in the amount of corrosion and rust that will occur and the amount of inhibitor required to prevent it. Longer service life, higher service temperatures, and higher molecular weight phosphorus-containing additives may require larger amounts of the inhibitor. In practice, this typically corresponds to a concentration of from 0.1 to 10.0% by weight, and preferably 1.0 to 3.0% by weight, of the anticorrosion and antirust additives of this invention. So long as about 0.1% by weight of the inhibitor is present, a significant amount of corrosion and rust inhibition is obtained. As the amount of inhibitor is increased, decreasing corrosion and rusting occurs up to about a 2% concentration of the inhibitor. Concentrations higher than about 2% seldom produce any increase in effect. The additive may be added at the point of use, but is preferably added during manufacture or packaging of the perfluoropolyether fluid, when appropriate quality control is more likely to be available.

Representative perfluoropolyethers having neutral end groups, utilizable for the formulation of oils and greases are available on the market under the trade-names FOMBLIN (from Ausimont, Milan, Italy), KRYTOX (from E. I. du Pont de Nemours and Company, Wilmington, Delaware), and DEMNUM (from Daikin, Osaka, Japan).

A grease based on perfluoropolyethers is typically composed of 15% to 40% by weight of polytetrafluoroethylene, which acts as a thickening agent, and 60% to 85% by weight of a liquid perfluoropolyether, together with minor

amounts of other products, such as perfluoroalkyl surfactants or polyoxyperfluoroalkyl surfactants, or other additives known in the art, such as stabilizers, anticorrosive agents, anti-wear agents etc. Additives of this type are also usually included in oils based on perfluoropolyethers.

- 5 Having described the invention, it will further be illustrated, but not limited, by the following examples.

EXAMPLES

MATERIALS

- 10 Phosphorus trichloride, phenylphosphonic dichloride, 4-nitrophenyl phosphorodichloridate, 4-chlorophenyl dichlorophosphate and the phenyl ester of phosphorodichloridic acid are available from chemical supply houses such as Aldrich Chemical Company, Milwaukee, Wisconsin. Other phosphorus reagents can be prepared using the same techniques as described above.

- 15 Hexafluoropropylene oxide acid fluorides $[F(CF(CF_3)CF_2O)_nCF(CF_3)COF]$ having $n = 1, 2,$ and 3 are available from PCR Inc., Gainesville, Florida. The trimer alcohol, $F[CF(CF_3)CF_2O]_3CF(CF_3)CH_2OH$ is also available from PCR Inc. Other perfluoroalkyl ether based alcohols, such as Ausimont's MF402 for the monofunctional alcohol, and FOMBLIN Z-Dol, Z-Dol 4000, Z-Dol TX, are also available.

- 20 KRYTOX oils and greases are available from E. I. du Pont de Nemours and Company, Wilmington, Delaware. FOMBLIN Oils and Greases are available from Ausimont USA Inc., Thorofare, New Jersey or Daiken Industries, Ltd., Chemical Division, Osaka, Japan.

- 25 Fluoroalcohols of the structure $F(CF_2)_q(CH_2)_2OH$ are available from E. I. du Pont de Nemours and Company as mixtures having $q = 2, 4, 6, 8,$ and 10 or as individual homologues following distillation.

TEST METHODS

Test Method 1—Rust/Corrosion Testing Procedure (ASTM (American Society for Testing Materials) D-665 Modified as described)

The coupons are cleaned in toluene or Stoddard solvent using a sonicator
5 for 15 minutes. They are then stored in a sealed container filled with fresh solvent
and soaked in a fluorochemical solvent such as VERTREL XF
(1,1,1,2,3,4,4,5,5,5-decafluoropentane, available from E. I. du Pont de Nemours
and Company, Wilmington, Delaware) for at least 5 minutes. The coupon is then
air-dried for 10 minutes. Contamination before use is avoided. The coupons are
10 coated thoroughly by dipping for 1 minute in the solution to be tested. Excess
solution is allowed to drain for 1 hour. The coupons are placed into a beaker of
medium hard water (see below) held at 80°C. The volume is adjusted to have the
coupons half immersed in the solution. The test is continued for 24 hours,
recording any rust formation. The test coupons are removed from the solution,
15 wiped with a paper towel to remove loose rust, and given a final evaluation.

The test coupons are C1018 Centerless ground cylindrical coupons having
1/4" diameter x 2-1/2" length (0.64 cm diameter and 6.35 cm length), with 1/16"
slot (0.16 cm slot), part # 2200 from Metal Samples Co., Munford Alabama.

Medium hard water (MIL-I-25017E) is prepared using three stock
20 solutions, 16.4 g/l sodium bicarbonate, 13.2 g/l anhydrous calcium chloride, and
8.2 g/l anhydrous magnesium sulfate. Sodium bicarbonate stock solution (10 ml)
is pipetted into 800 ml distilled water in a one liter volumetric flask, and shaken
vigorously. While swirling the contents of the flask, calcium chloride stock
solution (10 ml) and then 10 ml of the magnesium sulfate stock solution are
25 pipetted into the flask, distilled water is added to bring the volume to one liter, and
the solution mixed thoroughly. The final blend shall be clear and free of
precipitation.

Evaluations:

Excellent: no rust or light rust in a 24-hour period.
30 Good: moderate rust occurring in a 24-hour period.

Fair: severe rust occurring in a 24-hour period, but not covering over 35% of the surface of the specimen.

Poor: rust covering over 35% of the surface of the specimen (i.e., additive does practically nothing to prevent rust).

5 Results are shown in Table 1.

Test Method 2—Wear Testing (4-Ball, Cameron-Plint, and Load to Failure)

Wear testing was done in accordance with ASTM D-4172 for the 4-ball wear test and according to Cameron-Plint Tribology, Wokingham, England, producers of the Cameron-Plint tester. The Load to Failure (Pin on V-Block) Test
10 was run according to ASTM D-3233. Results are shown in Tables 2, 3, and 4.

Test Method 3—Oxidative Stability

The oxidative stability of the additive was tested using the Micro-Oxidation Test described in Tribology Transactions, V38(3), (1995), 618-626. Results are shown in Table 3.

15

EXAMPLES

Example 1a—Preparation of Methyl Ester

Into a 12-liter 3-neck flask fitted with a mechanical stirrer, thermocouple, and addition funnel is placed 1738.14 g of $F(CF(CF_3)CF_2O)_nCF(CF_3)COF$, having $n = 2$ to 16. With cooling of the reactor, 347 g anhydrous methanol is added. A
20 mildly exothermic reaction takes place and, after stirring for one hour, the methyl ester, $F(CF(CF_3)CF_2O)_nCF(CF_3)COOCH_3$, is washed with water to remove excess methanol and hydrogen fluoride. Final neutralization is effected by filtration through a column containing calcium carbonate and alumina. The yield is 1531 g of methyl ester.

Example 1b—Preparation of Perfluoroether Alcohol

Into a 5-liter 3-neck flask fitted with a mechanical stirrer, thermocouple, and addition funnel are placed 1569 g of isopropyl alcohol and 64.9 g of sodium borohydride. This mixture is cooled to 10°C and 1568 g of the methyl ester, $F(CF(CF_3)CF_2O)_nCF(CF_3)COOCH_3$, prepared as in Example 1a, is added. The mixture is refluxed at 83°C for 4 hours. After cooling to room temperature the excess sodium borohydride is decomposed with 20% ammonium chloride solution, washed with 10% saline and acetone, and dried to yield 1300 g of $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$, having $n = 2$ to 16.

Example 1c—Preparation of Perfluoroether Phosphate

Into a 6-liter 3-neck flask fitted with a mechanical stirrer, thermocouple, and two addition funnels are placed 388.7 g of $C_6H_5OP(O)Cl_2$ and 1,000 ml of FREON 113 (1,1,2-trichlorotrifluoroethane). Simultaneously 2,000 g of the alcohol $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$, prepared according to Example 1b, and 204.6 g of triethylamine are added to the flask while keeping the temperature below 15°C. After all of the reagents are added, the mixture is allowed to warm to room temperature and held at that temperature for 1 hour. Finally 5,000 g of water are introduced into the flask through an addition funnel and the mixture stirred for 4 hours. The product is washed with 2N dilute hydrochloric acid 3 times and then with sufficient acetone to break the emulsion. The mixture is split into 2 equal portions. Half was stored for use in Example 2. The solvent was removed from the remainder by vacuum distillation at 100°C and 1 mm Hg pressure (133 Pa) to yield 1050 g of product. Multi-nuclear NMR analysis shows the compound to be $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)[OH]OC_6H_5$.

Example 2—Preparation of Sodium Perfluoroether Phosphate

$F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)[OH]OC_6H_5$, 1050 g, prepared according to Example 1c, was placed in a 2-liter 3-neck flask fitted with a mechanical stirrer and thermocouple. To this mixture is added sufficient saturated sodium carbonate solution to insure the mixture has a $pH > 7$. The product is

washed 3 times with water to remove base and salt and the solvent removed as above. Multi-nuclear NMR and elemental analysis shows the compound to be $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)[ONa]OC_6H_5$.

Example 3—Preparation of Perfluoroether Phosphate

- 5 Into a 1.5-liter 3-neck flask fitted with a mechanical stirrer, thermocouple, and two addition funnels are placed 13.26 g of phenylphosphonic dichloride and 50 ml of FREON 113 (1,1,2-trichlorotrifluoroethane). After cooling with an ice water bath, 100 g of alcohol prepared according to Example 1b is added simultaneously with 7.21 g of triethylamine, keeping the temperature below 15°C.
- 10 After all of the reagents are added, the mixture is allowed to warm to room temperature and held at that temperature for 1 hour. Finally 1,000 g of water are introduced into the flask through an addition funnel and the mixture stirred for four hours. The product is washed with a mixture of 1% saline and acetone. Product, 103 g, was recovered. Multi-nuclear NMR analysis following solvent removal
- 15 shows the compound to be $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)[OH][C_6H_5]$.

Example 4—Preparation of Sodium Perfluoroether Phosphate

- Into a 100-milliliter 3-neck flask fitted with a mechanical stirrer, are placed 20.0 g of $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)[OH][C_6H_5]$, prepared according to Example 3, along with 20 ml of FREON 113 (1,1,2-trichlorotrifluoroethane). To
- 20 this mixture is added sufficient 1 M saturated sodium carbonate solution to insure the mixture has a pH greater than 7. The product is washed 3 times with water to remove base and salt and the solvent removed as above. Multi-nuclear NMR and elemental analysis following solvent removal shows the compound to be $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)[ONa][C_6H_5]$.

Example 5—Preparation of Perfluoroether Phosphate with Aryl Substituent (NO₂)

Into a 200-milliliter 3-neck flask fitted with a mechanical stirrer, thermocouple, and two addition funnels are placed 12.05 g of 4-nitrophenyl phosphorodichloridate and 75 ml of FREON 113 (1,1,2-trichlorotrifluoroethane).

After cooling with an ice water bath, 50 g of the alcohol

$F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$, prepared according to Example 1b, is added followed by 4.03 g of pyridine while keeping the temperature below 15°C. After all of the reagents are added, the mixture is allowed to warm to room temperature and held at that temperature for 1 hour. Finally 500 g of water are introduced into the flask through an addition funnel and the mixture stirred for four hours. The product is washed with a mixture of 1% saline and acetone. Multi-nuclear NMR analysis following solvent removal shows the compound to be $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)(OH)[p-OC_6H_4NO_2]$.

10 **Example 6—Preparation of Perfluoroether Phosphate with Pentafluorophenyl Ester Group**

Into a 250-milliliter 3-neck flask fitted with a mechanical stirrer, thermocouple, and addition funnel are placed 9.02 g pentafluorophenol, 7.52 g phosphorus oxychloride and 75 ml FREON 113 (1,1,2-trichlorotrifluoroethane).

15 After cooling the mixture with an ice water bath, 3.87 g of pyridine is slowly added to the flask, the product stirred for 1 hour, and warmed to room temperature. Then 50 g of the alcohol $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$, prepared according to Example 1b, is added, followed by 4.03 g of pyridine, while keeping the temperature below 15°C. After all of the reagents are added, the mixture is allowed

20 pentafluorophenyl to warm to room temperature and held at that temperature for 1 hour. Finally 500 g of water are introduced into the flask through an addition funnel and the mixture stirred for four hours. The product is washed with a mixture of 1% saline and acetone. Multi-nuclear NMR analysis following solvent removal shows the compound to be $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OP(O)(OH)[OC_6F_5]$.

25 **Example 7—Preparation of Perfluoroether Phosphate with Aryl Substituent (Cl)**

Into a 200-milliliter 3-neck flask fitted with a mechanical stirrer, thermocouple, and two addition funnels are placed 11.44 g of p-chlorophenyl dichlorophosphate and 75 ml of FREON 113 (1,1,2-trichlorotrifluoroethane).

30 After cooling with an ice water bath, 50 g of the alcohol $F(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$, prepared according to Example 1b, is added

followed by 4.03 g of pyridine while keeping the temperature below 15°C. After all of the reagents are added, the mixture is allowed to warm to room temperature and held at that temperature for 1 hour. Finally 500 g of water are introduced into the flask through an addition funnel and the mixture stirred for four hours. The product is washed with a mixture of 1% saline and acetone. Multi-nuclear NMR analysis following solvent removal shows the compound to be

$$\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n\text{CF}(\text{CF}_3)\text{CH}_2\text{OP}(\text{O})[\text{OH}][p\text{-OC}_6\text{H}_4\text{Cl}].$$

Example 8—Preparation of Perfluorohexylethyl Phosphate

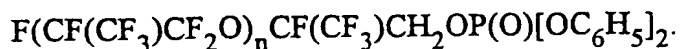
Into a 100-milliliter 3-neck flask fitted with a mechanical stirrer, thermocouple, and an addition funnel are placed 26.59 g of phenyl dichlorophosphate and 50 g 1H,1H,2H,2H-perfluorooctanol. After all of the reagents are added, the mixture is warmed about 130°C to 150°C for 16 hours and hydrogen chloride is evolved. Finally, following cooling to less than 50°C, 100 g of water are introduced into the flask through an addition funnel and the mixture heated to 95°C for one hours. FREON 113 (1,1,2-trichlorotrifluoroethane) is introduced into the cooled flask and the product is washed with 2% saline and residual water removed at 100°C and 1 mm Hg pressure (133 Pa). Multi-nuclear NMR analysis following solvent removal shows the compound to be

$$(\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{O})_{1.2}\text{P}(\text{O})[\text{OH}]_{0.8}[\text{OC}_6\text{H}_5].$$

Example 9—Preparation of a Fully Esterified Perfluoroether Phosphate

Into a 250-milliliter 3-neck flask fitted with a mechanical stirrer, thermocouple, and an addition funnel are placed 13.31 g of diphenyl chlorophosphate and 50 ml of FREON 113 (1,1,2-trichlorotrifluoroethane). After cooling with an ice water bath, 50 g of the alcohol, $\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$, prepared according to Example 1b, is added followed by 4.03 g of pyridine while keeping the temperature below 15°C. After all of the reagents are added, the mixture is allowed to warm to room temperature and held at that temperature for 1 hour. Finally, 500 g of water are introduced into the flask through an addition funnel and the mixture stirred for four hours. The product is washed with a mixture of 1% saline and acetone. Multi-nuclear

NMR analysis following solvent removal shows the compound to be



Example 10—Preparation of a Perfluoroether Phosphate

Into a 500-milliliter 3-neck flask fitted with a mechanical stirrer,
5 thermocouple, and an addition funnel are placed 48.6 g of phenyl
dichlorophosphate and 250 g of the alcohol $\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$,
prepared according to Example 1b. After all of the reagents are added, the mixture
is warmed to about 130°C for 16 hours and hydrogen chloride is evolved. Finally,
following cooling to less than 50°C, 100 g of water are introduced into the flask
10 through an addition funnel and the mixture heated to 95°C for one hours. The
product is washed with a mixture of 1% saline and acetone and residual water
removed at 100°C and 1 mm Hg pressure (133 Pa). Multi-nuclear NMR analysis
following solvent removal shows the compound to be
 $\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n\text{CF}(\text{CF}_3)\text{CH}_2\text{OP}(\text{O})[\text{OH}][\text{OC}_6\text{H}_5].$

Table 1**Rust/Corrosion Test Results (Test Method 1)**

Ex. #	Control Test Description	ASTM Method Corrosion Test			
Control Tests with no additive:					
D	Bare pin, no oil	Poor			
E	Pin and oil, without additive	Poor			
Ex. #	Additive Structure	Compat- ibility with NaNO ₂ *	ASTM Method Corrosion Test Additive Conc.*		
			0.5%	1.0%	2.0%
Comparative Examples from the prior art:					
A	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH) ₂ (from Borecki, US 3,306,855)	Poor	Fair	Fair	Fair
B	{F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ O} ₂ P[O](OH) (from Borecki, US 3,306,855)	Poor	Poor	Poor	Poor
C	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)COOH (from Skehan, US 3,367,868)	Poor	NA	NA	Good
Examples:					
1c	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH)(OC ₆ H ₅)	Poor	Fair	Good	Excl
2	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](ONa)(OC ₆ H ₅)	Excl	NA	Excl	Excl
3	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH)(C ₆ H ₅)	Poor	Fair	Good	Excl
4	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](ONa)(C ₆ H ₅)	Excl	NA	Fair	Fair
5	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH)(p-OC ₆ H ₄ NO ₂)	Poor	NA	NA	Excl
6	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH)(OC ₆ F ₅)	Poor	NA	NA	Excl
7	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH)(p-OC ₆ H ₄ Cl)	Poor	NA	NA	Excl
8	F(CF ₂) ₆ C ₂ H ₄ OP[O](OH)(OC ₆ H ₅)	Poor	NA	NA	Excl
9	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OC ₆ H ₅) ₂	Good	NA	NA	Excl
10	F[CF(CF ₃)CF ₂ O] ₍₄₋₁₀₎ CF(CF ₃)CH ₂ OP[O](OH)(OC ₆ H ₅)	Poor	Fair	Good	Excl

*Excl = Excellent, NA = not applicable/not tested.

Table 1 indicates Comparative Examples A to C from the prior art show inferior protection compared with Examples 1c to 10 of the present invention. Examples 1c to 3 and 5 to 10 show excellent performance at the 2% loading. Examples 2, 4, and 9 (sodium salt compositions) show good to excellent compatibility with NaNO_2 . Immediate rusting occurs with no additives or oil alone (Controls D and E)

Table 2

ASTM-3233 Pin on V-Block Tests (Test Methods 2)

Sample Description	Load, lb (kg)	Torque, in-lbf (N-m)
KRYTOX GPL-105 Base Oil	3,000 (1,361)	96 (10.8)
2% $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_{(4-10)}\text{CF}(\text{CF}_3)\text{CH}_2\text{OP}[\text{O}](\text{OH})(\text{OC}_6\text{H}_5)$ (2% additive from Example 1c)	3,000 (1,361)	50 (5.6)

In this load-to-failure test, both samples passed the maximum 3,000 lb (1,361 kg) part of the test. However, the improved performance of the oil containing the additive is shown in the reduced torque required. Additionally, the wear scar width measured on the V-block used with the formulated oil was only about 0.5 mm versus a much higher value of about 1.25 mm for the V-block used with the non-formulated (base) oil. Visually, the pins and V-blocks from the base oil test had acquired a blue-violet color, indicating a high heat flux in the parts. Pins and V-blocks from the test using the oil with the additive of Example 1c, however, were only slightly amber in color, indicating a substantially lower operating temperature during the test.

Table 3**4-Ball Wear Test (Test Method 2).**

Sample Description	Wear Scar (mm)
DEMNUM S-65 Base Oil	1.52
$F[CF(CF_3)CF_2O]_{(4-10)}CF(CF_3)CH_2OP[O](OH)(OC_6H_5)$ (1% Additive from Example 1c)	0.66
Conditions: immersed in the lubricant, at 75°C and under a 40 kg load, 1200 rpm for 2 hours, with dry N ₂ sweep.	

Table 3 shows improved wear over the unformulated base oil.

Table 4**Cameron-Plint Wear Data (Test Methods 2)**

Sample Description	Wear Scar (mm)
DEMNUM S-65 Base Oil	2.24
1% $F[CF(CF_3)CF_2O]_{(4-10)}CF(CF_3)CH_2OP[O](OH)(OC_6H_5)$ (1% additive from Example 1c)	0.89
Cameron-Plint oscillatory wear test conditions: M-50 Steel, 6 mm by 6 mm length pin, Rc60 on M-50 Steel, 24 mm diameter disk at 150°C at 6 Hz with 9 mm stroke length for 2 hours.	

Table 4 shows improved wear over the unformulated base oil.

Table 5**Micro-Oxidation Stability Results (Test Method 3)**

°C	DEMNUM S-65 Base Oil	Additive of Example 1c $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_{(4-10)}\text{CF}(\text{CF}_3)\text{CH}_2\text{OP}[\text{O}](\text{OH})(\text{OC}_6\text{H}_5)$
290	Pass	Pass
300	Fail	Pass
315		Pass
330		Pass
345		Marginal Pass
360		Fail

Table 5 shows a 55°C improvement in base oil stability using oil formulated with the additive of Example 1c.

WHAT IS CLAIMED IS:

1. Partially esterified aryl phosphates and phosphonates, and salts thereof, containing either (i) a mono- or poly-alkylene oxide linking group between the phosphorus and a fluorocarbon group, or (ii) no linking group between the phosphorus and fluorocarbon group;
2. Compounds of claim 1 having Formula I as defined in the specification.
3. Compounds of claim 1 having Formula II as defined in the specification.
4. Compounds of claim 1 having Formula III as defined in the specification.
5. Compounds of claim 1 having Formula IV as defined in the specification.
6. Compounds of claim 1 having Formula V as defined in the specification.
7. Compounds of claim 1 having Formula VI as defined in the specification.
8. Asymmetrical fully substituted compounds being either (i) aryl phosphites or phosphates containing a mono or poly alkylene oxide linking group between the phosphorus and a perfluoroether group, or (ii) aryl phosphines, phosphinites, phosphonites, phosphine oxides, phosphinates or phosphonates with no linking group between the phosphorus and a fluorocarbon group.
9. Compounds of claim 8 having Formula VII as defined in the specification.
10. Compounds of claim 8 having Formula VIII as defined in the specification.
11. Compounds of claim 8 having Formula IX as defined in the specification.
12. Compounds of claim 8 having Formula X as defined in the specification.

13. Compounds of claim 8 having Formula XI as defined in the specification.

14. Salts of partially esterified aryl phosphates having an aryl group between the phosphorus and a fluorocarbon.

5 15. Compounds of claim 14 having Formula XII as defined in the specification.

16. A perfluoropolyether oil or grease containing 0.1 to 10% by weight of an aryl phosphorus compound selected from the group consisting of:

10 A. Partially esterified aryl phosphates and phosphonates, and salts thereof, containing either (i) a mono- or poly-alkylene oxide linking group between the phosphorus and a fluorocarbon group, or (ii) no linking group between the phosphorus and fluorocarbon group;

15 B. Asymmetrical fully substituted compounds being either (i) aryl phosphites or phosphates containing a mono or poly alkylene oxide linking group between the phosphorus and a perfluoroether group, or (ii) aryl phosphines, phosphinites, phosphonites, phosphine oxides, phosphinates or phosphonates with no linking group between the phosphorus and a fluorocarbon group.

20 C. Salts of partially esterified aryl phosphates having an aryl group between the phosphorus and a fluorocarbon.

25 17. The perfluoropolyether oil or grease of claim 16 containing 0.1 to 3% by weight of at least one partially esterified aryl phosphate and phosphonate, or salts thereof, containing either (i) a mono- or poly-alkylene oxide linking group between the phosphorus and a fluorocarbon group, or (ii) no linking group between the phosphorus and fluorocarbon group.

18. The composition of claim 17 wherein said aryl phosphorus compound has Formula I as defined in the specification.

19. The composition of claim 17 wherein said aryl phosphorus compound has Formula II as defined in the specification.

20. The composition of claim 17 wherein said aryl phosphorus compound has Formula III as defined in the specification.

5 21. The composition of claim 17 wherein said aryl phosphorus compound has Formula IV as defined in the specification.

22. The composition of claim 17 wherein said aryl phosphorus compound has Formula V as defined in the specification.

10 23. The composition of claim 17 wherein said aryl phosphorus compound has Formula VI as defined in the specification.

24. The perfluoropolyether oil or grease composition of claim 16 containing 0.1 to 3% by weight of at least one asymmetrical fully substituted compound being either (i) aryl phosphites or phosphates containing a mono or poly alkylene oxide linking group between the phosphorus and a perfluoroether group,
15 or (ii) aryl phosphines, phosphinites, phosphonites, phosphine oxides, phosphinates or phosphonates with no linking group between the phosphorus and a fluorocarbon group.

25. The composition of claim 24 wherein said aryl phosphorus compound has Formula VII as defined in the specification.

20 26. The composition of claim 24 wherein said aryl phosphorus compound has Formula VIII as defined in the specification.

27. The composition of claim 24 wherein said aryl phosphorus compound has Formula IX as defined in the specification.

25 28. The composition of claim 24 wherein said aryl phosphorus compound has Formula X as defined in the specification.

29. The composition of claim 24 wherein said aryl phosphorus compound has Formula XI as defined in the specification.

30. The composition of claim 24 wherein said aryl phosphorus compound has Formula XII as defined in the specification.

31. The perfluoropolyether oil or grease composition of claim 16 containing 0.1 to 3% by weight of at least one salts of a partially esterified aryl phosphates having an aryl group between the phosphorus and a fluorocarbon.

32. The composition of claim 29 wherein said aryl phosphorus compound has Formula XII as defined in the specification.

INTERNATIONAL SEARCH REPORT

Inte. nat Application No
PCT/US 99/06816

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F9/12 C10M137/02 C10M137/12 C10M169/04 C07F9/40
C07F9/32 C07F9/53 C07F9/50 C07F9/46 C07F9/48
/(C10M169/04, 107:38, 137:02, 137:12)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 337 655 A (CHRISTIAN A. SEIL) 22 August 1967 see the whole document ---	1
X	US 3 308 207 A (CHRISTIAN A. SEIL) 7 March 1967 see the whole document ---	1
X	US 3 308 208 A (CHRISTIAN A. SEIL) 7 March 1967 see the whole document ---	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

31 May 1999

Date of mailing of the international search report

10/06/1999

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Authorized officer

Beslier, L

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NN.V. PAVLENKO: "Esters of bis(perfluoroalkyl)phosphinic acids" JOURNAL OF GENERAL CHEMISTRY USSR., vol. 59, no. 3, - 20 August 1989 pages 474-476, XP002104254 NEW YORK US see table 1, compound VI ---	8,10
A	US 3 367 868 A (JOHN TEVLIN SKEHAN) 6 February 1968 cited in the application see the whole document ---	1-32
A	US 5 550 277 A (KAZIEMIRA J.L. PACIOREK) 27 August 1996 cited in the application see the whole document ---	1-32
A	US 3 306 855 A (WILLIAM J. BORECKI) 28 February 1967 cited in the application see the whole document -----	1-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/06816

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3337655	A	22-08-1967	NONE	
US 3308207	A	07-03-1967	NONE	
US 3308208	A	07-03-1967	NONE	
US 3367868	A	06-02-1968	NONE	
US 5550277	A	27-08-1996	NONE	
US 3306855	A	28-02-1967	NONE	

